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Mechanism of Operation of the TFE-Bonded Gas-Diffusion Electrode

A mathematical analysis has been made of a proposed working mechanism of the TFE (polytetrafluoroethylene)-bonded gas-diffusion electrode used in fuel cells. A mathematical analytical model is used to predict the performance of the electrode as a function of such measurable physical characteristics as intrinsic activity of catalyst; size of porous, electrically conductive agglomerates consisting of catalyst particles; internal porosity; and real surface area. An oxygen electrode in an alkaline electrolyte is used as an example for application of the mathematical analytical model.

The proposed working mechanism of the TFE-bonded electrode is based on a concept in which it is assumed that the catalyst particles form porous electrically conductive agglomerates which are completely flooded with electrolyte. The agglomerates are kept together by the TFE binder which creates hydrophobic gas channels. As current is drawn from the electrode, reactant gas diffuses through the channels, dissolves in the electrolyte contained in the agglomerates, and the solution diffuses to the center of the agglomerates, with simultaneous reaction along this diffusion path. For the mathematical treatment, the proposed model is simplified further by assuming cylindrical flooded agglomerates, with a continuous distribution of catalyst and electrolyte.

The following conclusions have been reached with the simplified mathematical model: (1) The model allows one to predict not only the utilization of the catalyst across the thickness of the electrode (transversal utilization), but also the utilization of the catalyst along the radius of the flooded agglomerate. As a consequence, in addition to often studied variables such as porosity and bulk surface area, the im-

portance of agglomerate size is shown. A parameter (q) which determines the radial current distribution in the agglomerate is introduced and quantitatively defined as a function of diffusion coefficient, microporosity, solubility of reactant gas, exchange current, bulk surface area, local potential, and agglomerate radius. (2) For the specific example of the oxygen reduction on TFE-bonded Pt electrodes in 30 percent KOH at 80°C, a good radial distribution is obtained for agglomerate sizes below 1 micron and polarizations up to 300 mV. Under similar conditions the transversal utilization of the electrode is very good (very low internal IR drops). (3) For the same example, the structures are poor (low microporosity and large agglomerate size), and both the radial utilization of agglomerates and the transversal utilization of the electrode become poor at higher current drains ($I > 300 \text{ mA/cm}^2$). (4) For good transversal utilization of the electrode and good radial utilization of the agglomerate, the Tafel plot for the porous electrode is the same as that obtained with a smooth electrode. If, on the other hand, the transversal utilization of the electrode is good but the radial utilization of the agglomerate is very poor, a linear relationship is predicted, with a Tafel slope twice that of the smooth electrode. (5) The model and, more specifically, the parameter of radial distribution can be used to design more efficient hydrophobic gas-diffusion electrodes by predicting the maximum tolerable agglomerate size. When due to a high ratio of diffusion to activation control for a certain electrode reaction, high values of q are obtained for all reasonable agglomerate sizes, the model suggests the use of porous, conductive agglomerates which have been activated with catalyst only on their periphery.

(continued overleaf)

(6) The model cannot be used without further modification to predict quantitatively the performance of hydrogen in acid electrolyte electrodes with high exchange current, because the parameter q becomes too large and the assumption of a continuum distribution of catalyst and electrolyte does not apply.

Note:

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Reference: NASA CR-97624 (N69-10585),
Development of Cathodic Electrocatalysts for Use in Low Temperature Hydrogen/Oxygen Fuel Cells with an Alkaline Electrolyte

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